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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Eugene B. LEVICH et al.

Confirmation No.: 8265

Patent No.: 6,960,426 B2

Application No.: 09/886,979

Patent Date: November 1, 2005

Filing Date: January 15, 2002

For: SILVER HALIDE MATERIAL FOR
OPTICAL MEMORY DEVICES WITH
LUMINESCENT READING AND
METHODS FOR THE TREATMENT
THEREOF

Attorney Docket No.: 85134-4999

**REQUEST FOR CERTIFICATE OF CORRECTION
UNDER 37 C.F.R. §§ 1.322 and 1.323**

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Certificate
DEC 08 2005
of Correction

Sir:

Patentees hereby respectfully request the issuance of a Certificate of Correction in connection with the above-identified patent. The corrections are listed on the attached Form PTO-1050. The corrections requested are as follows:

Column 16:

Line 41 (claim 4, line 6), change "[FeCN]₆⁻³" to -- [Fe(CN)₆]⁻³ --. Support for this change appears in application claim 75.

Line 57 (claim 5, line 12), change "K₃[Fe(CN)₆], (NH₄)₂S₂O₈" to -- K₃[Fe(CN)₆], (NH₄)₂S₂O₈ --. Support for this change appears in application claim 5.

Line 61 (claim 5, line 16), change "[FeCN₆]⁻³" to -- [Fe(CN)₆]⁻³ --. This change is requested merely to correct a typographical error.

Column 17:

Line 67 (claim 13, line 6), change "[FeCN₆]⁻³" to -- [Fe(CN)₆]⁻³ --. This change is requested merely to correct a typographical error.

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Column 18:

Line 43 (claim 17, line 4), change "canied" to -- carried --. Support for this change appears in application claim 73.

Line 45 (claim 17, line 6), change "[FeCN₆]⁻³" to -- [Fe(CN)₆]⁻³ --. This change is requested merely to correct a typographical error.

Column 20:

Line 6 (claim 21, line 6), change "[FeCN₆]⁻³" to -- [Fe(CN)₆]⁻³ --. This change is requested merely to correct a typographical error.

The requested changes are to correct errors of a clerical or typographical nature and do not involve changes that would constitute new matter or require reexamination.

A fee of \$100 is believed to be due for this request. Please charge the required fees to Winston & Strawn LLP Deposit Account No. 50-1814. Please issue a Certificate of Correction in due course.

Respectfully submitted,

12/6/05
Date

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212-294-3311

UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO.: 6,960,426 B2
DATED: November 1, 2005
INVENTORS: Levich et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 16:

Line 41 (claim 4, line 6), change "[FeCN]₆⁻³" to -- [Fe(CN)₆]⁻³ --.

Line 57 (claim 5, line 12), change "K₃[Fe(CN)₆], (NH₄)₂S₂O₈" to -- K₃[Fe(CN)₆], (NH₄)₂S₂O₈ --.

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15

1,1',1'',3,3'-hexamethylindocarbocyanineiodide was adsorbed from a 1.0×10^{-5} M water alcohol (1:1) solution on formed silver salt of 2-mercaptobenzothiazole. The places where there are particles with adsorbed salt do not luminesce and there was luminescence from the bulk polymer. The dye has an absorption λ_{max} 650 nm and luminescence λ_{max} 682 nm.

EXAMPLE 20

The same as in Example 11, except that after bleaching, the layer was treated with 0.1% solution of $\text{Ga}(\text{NO}_3)_3$ washed with water and treated with 0.05% solution of 8-oxiquinoline. The dye was adsorbed on the insoluble salts that were located at the places where the photolayer was exposed to light. The adsorbed dye was luminescing in the yellow-green range of spectrum.

EXAMPLE 21

The same as in the Example 20, except that after bleaching, the exposed photolayer was treated with 0.1% solution of $\text{Cu}(\text{NO}_3)_2$ washed with water and treated with 0.2% water solution of methylcalcein. In the places where the photolayer was exposed to light and the copper salt had absorbed the dye had a yellow-green luminescence and the background was not luminescent.

EXAMPLE 22

Similarly to the Example 1, the AgBr emulsion was prepared and was divided into three parts. The first part of the emulsion was spectrally sensitized as in Example 4, the second part of the emulsion was spectrally sensitized as in Example 7 and the third one, as in Example 8. The sensitized emulsions were coated using a multi-slit filler by layers on to the gelatine coated polyethylene terephthalate base. For the information recording the photomaterial consistently exposed through the mask following the light filters, transmitting light with a wavelength of 860 nm, 680 nm and 545 nm. The photolayers were subjected to the photo-chemical treatment as in the Example 18 and with a 0.001% water solution of the sodium salt of 1,1'-di- γ -sulfopropyl-5,5'-disulfo-3,3',3''-tetramethylindocarbocyaninebetaine. The luminescence maximum of the absorbed dye was 700 nm.

EXAMPLE 23

The same as in the Example 22, except that the treatment of layers was conducted with 0.001% water solution of trisodium salt of 1,1'-di- γ -sulfopropyl 5,5'-disulfo-3,3',3''-tetramethyl-n-indotricarbocyaninebetaine. The maximum of luminescence -790 nm.

EXAMPLE 24

The silver halide systems are characterized of high photostability. The irradiation of the film obtained in Example 22, for 200 hours in a cuvette of a Shimadzu spectrofluorimeter at a wavelength of 640 nm used for fluorescent excitability did not lead to any changes in the fluorescent intensity. During similar film irradiation, based on the bis-dianilinochloromethyl-1,3,4-oxadiazole as in the U.S. Pat. No. 3,869,363, a decrease of the fluorescent intensity of 2.5 times was observed.

Although certain presently preferred embodiments of the present invention have been specifically described herein, it will be apparent to those skilled in the art to which the invention pertains that variations and modifications of the

16

various embodiments shown and described herein may be made without departing from the spirit and scope of the invention. Accordingly, it is intended that the invention be limited only to the extent required by the appended claims and the applicable rules of law.

What is claimed is:

1. A digital optical memory device comprising:

(a) a digital optical memory medium comprising a plurality of layers of a luminescent material for an optical digital memory device, each of said plurality of layers comprising insoluble microparticles dispersed in a water soluble polymer, said microparticles having a particle size less than 0.2 microns, said microparticles having a sorbed luminescent dye, said insoluble microparticles comprising silver microparticles and insoluble metal salts, said silver microparticles being a product of oxidation of silver; and

(b) a two-laser system for two photon writing data in digital form on said digital optical memory medium.

2. The device of claim 1, wherein the luminescent dye is selected from the group consisting of xanthene dyes, acridine dyes, oxazine dyes, indigo dyes, polycyclic vat dyes, benzanthrone in the form of sulfuric esters of leuco compounds, dyes form both luminescent and non-luminescent complexes with polyvalent metal ions, and cyanine dyes.

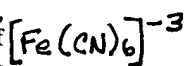
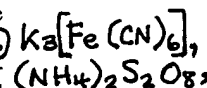
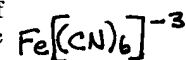
3. The device of claim 1 wherein the microcrystals have a size of about 0.02 to 0.08 microns and wherein the water soluble polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, gelatin modified with polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl sulphate, carboxymethylcellulose, cellulose acetophthalate, phthaloylgelatin or graft polymers of gelatin with polymethoxydiethyleneglycol acrylate, polydiaceto-neacrylamide or poly-N,N'-methylenediacrylamide, and mixtures thereof.

4. The device of claim 1, wherein the silver microparticles are oxidized by an oxidizer selected from the group consisting of $\text{K}_3[\text{Fe}(\text{CN})_6]$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KMnO_4 , CuCl_2 , FeCl_3 and quinones, and said oxidation being carried out in a presence of anions selected from the group consisting of SCN^- , CN^- , $\text{Cr}_2\text{O}_7^{2-}$, WO_4^{2-} , $[\text{Fe}(\text{CN})_6]^{3-}$, oxalate, citrate and anions of 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and organic mercapto compounds.

5. A digital optical memory device comprising:

(a) a digital optical memory medium comprising a plurality of layers of a luminescent material for an optical digital memory device, each of said plurality of layers comprising insoluble microparticles dispersed in a water soluble polymer, said microparticles having a particle size less than 0.2 microns, said microparticles having a sorbed luminescent dye, said insoluble microparticles comprising silver microparticles and insoluble metal salts, said silver microparticles being a product of oxidation of silver by an oxidizer selected from the group consisting of $\text{K}_3[\text{Fe}(\text{CN})_6]$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KMnO_4 , CuCl_2 , FeCl_3 and quinones, and said oxidation being carried out in a presence of anions selected from the group consisting of SCN^- , CN^- , $\text{Cr}_2\text{O}_7^{2-}$, WO_4^{2-} , $[\text{Fe}(\text{CN})_6]^{3-}$, oxalate, citrate and anions of 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and organic mercapto compounds; and

(b) a two-laser system for two photon writing data in digital form on said digital optical memory medium.



17

6. The memory device of claim 5, wherein the two-laser system comprises means for two-photon writing of the data in a three dimensional optical matrix in said digital optical memory medium.

7. The memory device of claim 5 wherein at least one of said plurality of layers has data stored in digital form therein; and the device further comprises means for reading said data in said digital form from said digital optical memory medium.

8. The device of claim 5, wherein the luminescent dye is selected from the group consisting of xanthene dyes, acridine dyes, oxazine dyes, indigo dyes, polycyclic vat dyes, benzantrones in the form of sulfuric esters of leuco compounds, dyes form both luminescent and non-luminescent complexes with polyvalent metal ions, and cyanine dyes.

9. The device of claim 5 wherein the microcrystals have a size of about 0.02 to 0.08 microns and wherein the water soluble polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, gelatin modified with polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl sulphate, carboxymethylcellulose, cellulose acetophthalate, phthaloylgelatin or graft polymers of gelatin with polymethoxydiethyleneglycol acrylate, polydiaceto-neacrylamide or poly-N,N'-methylenediacrylamide, and mixtures thereof.

10. A method of reading digital data comprising:

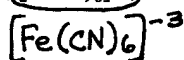
(a) providing a digital optical memory medium, the medium comprising a plurality of layers of a luminescent material for an optical digital memory device, each of said plurality of layers comprising insoluble microparticles dispersed in a water soluble polymer, said microparticles having a particle size less than 0.2 microns, said microparticles having a sorbed luminescent dye, said insoluble microparticles comprising silver microparticles and insoluble metal salts, said silver microparticles being a product of oxidation of silver, at least one of said plurality of layers having data stored in digital form therein from a two-laser system for two photon writing of such data in digital form on said digital optical memory medium; and

(b) reading said data in said digital form from said digital optical memory medium.

11. The method of claim 10, wherein the luminescent dye is selected from the group consisting of xanthene dyes, acridine dyes, oxazine dyes, indigo dyes, polycyclic vat dyes, benzantrones in the form of sulfuric esters of leuco compounds, dyes form both luminescent and non-luminescent complexes with polyvalent metal ions, and cyanine dyes.

12. The method of claim 10 wherein the microcrystals have a size of about 0.02 to 0.08 microns and wherein the water soluble polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, gelatin modified with polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl sulphate, carboxymethylcellulose, cellulose acetophthalate, phthaloylgelatin or graft polymers of gelatin with polymethoxydiethyleneglycol acrylate, polydiaceto-neacrylamide or poly-N,N'-methylenediacrylamide, and mixtures thereof.

13. The method of claim 10, wherein the silver micro-particles are oxidized by an oxidizer selected from the group consisting of $K_3[Fe(CN)_6]$, $(NH_4)_2S_2O_8$, $KMnO_4$, $CuCl_2$, $FeCl_3$ and quinones, and said oxidation being carried out in a presence of anions selected from the group consisting of SCN^- , CN^- , $Cr_2O_7^{2-}$, WO_4^{2-} , $[Fe(CN)_6]^{3-}$, oxalate, citrate



18

and anions of 1-phenyl-5-mercaptopotetrazole, 2-mercapto-bezothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and organic mercapto compounds.

14. A method of storing information on a digital optical memory medium, the method comprising:

forming a digital optical memory medium by:

simultaneously extruding, from a multi-slit filler, thin layers of photographic emulsion and between them thick layers of silver halide free polymer to a substrate to form a multi-layer material;

exposing said multi-layer material to light;

developing and fixation of said multi-layer material to form silver particles from the exposed silver halide;

oxidation of the silver particles to form the insoluble salt particles;

treating the multi-layer material with luminescing dye and allowing the luminescing dye to be sorbed onto the particles; and

writing data in digital form onto said medium a two-laser system for two photon writing of such data in digital form on said digital optical memory medium.

15. The method of claim 14, wherein the luminescent dye is selected from the group consisting of xanthene dyes, acridine dyes, oxazine dyes, indigo dyes, polycyclic vat dyes, benzantrones in the form of sulfuric esters of leuco compounds, dyes form both luminescent and non-luminescent complexes with polyvalent metal ions, and cyanine dyes.

16. The method of claim 14 wherein the microcrystals have a size of about 0.02 to 0.08 microns and wherein the water soluble polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, gelatin modified with polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl sulphate, carboxymethylcellulose, cellulose acetophthalate, phthaloylgelatin or graft polymers of gelatin with polymethoxydiethyleneglycol acrylate, polydiaceto-neacrylamide or poly-N,N'-methylenediacrylamide and mixtures thereof.

17. The method of claim 14, wherein the silver micro-particles are oxidized by an oxidizer selected from the group consisting of $K_3[Fe(CN)_6]$, $(NH_4)_2S_2O_8$, $KMnO_4$, $CuCl_2$, $FeCl_3$ and quinones, and said oxidation being carried out in a presence of anions selected from the group consisting of SCN^- , CN^- , $Cr_2O_7^{2-}$, WO_4^{2-} , $[Fe(CN)_6]^{3-}$, oxalate, citrate and anions of 1-phenyl-5-mercaptopotetrazole, 2-mercapto-bezothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and organic mercapto compounds.

18. A method of digitally storing information, the method comprising:

providing one or a plurality of layers comprising silver halide particles having a particle size less than about 0.2 microns;

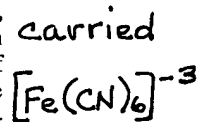
exposing at least one layer to light using two laser beams at at least one predetermined point of the layer(s);

developing and fixation of said exposed layer(s) to form silver particles from the exposed silver halide;

oxidizing the silver particles to form insoluble salt particles; and

treating the layer(s) with luminescing dye and allowing the luminescing dye to be sorbed onto the particles.

19. The method of claim 18, wherein the luminescent dye is selected from the group consisting of xanthene dyes, acridine dyes, oxazine dyes, indigo dyes, polycyclic vat dyes, benzantrones in the form of sulfuric esters of leuco



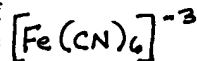
19

compounds, dyes form both luminescent and non-luminescent complexes with polyvalent metal ions, and cyanine dyes.

20. The method of claim 18 wherein the microcrystals have a size of about 0.02 to 0.08 microns and wherein the water soluble polymer is selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, gelatin modified with polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl sulphate, carboxymethylcellulose, cellulose acetophthalate, phthaloylgelatin or graft polymers of gelatin with polymethoxydiethyleneglycol acrylate, polydiaceto-
neacrylamide or poly-N,N'-methylenediacrylamide, and mixtures thereof.

20

21. The method of claim 18, wherein the silver micro-particles are oxidized by an oxidizer selected from the group consisting of $K_3[Fe(CN)_6]$, $(NH_4)_2S_2O_8$, $KMnO_4$, $CuCl_2$, $FeCl_3$ and quinones, and said oxidation being carried out in a presence of anions selected from the group consisting of SCN^- , CN^- , $Cr_2O_7^{2-}$, WO_4^{2-} , $[Fe(CN)_6]^{3-}$, oxalate, citrate and anions of 1-phenyl-5-mercaptotetrazole, 2-mercaptobezothiazole, 2-mercaptobenzoxazole, 2-mercaptobenzimidazole and organic mercapto compounds.



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